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PATENT SPECIFICATION

805,588



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COMPLETE SPECIFICATION

Method of Plasticizing Linear Aromatic Polyesters

1 We, THE GOODYEAR TIRE & RUBBER
COMPANY, a corporation organized under the
Laws of the State of Ohio, United States of
America, with offices at 1144 East Market
5 Street, Akron, Ohio, United States of
America, do hereby declare the invention, for
which we pray that a patent may be granted
to us, and the method by which it is to be
performed, to be particularly described in and
10 by the following statement:—

This invention relates to a method of
plasticizing linear aromatic polyesters.

15 High molecular weight linear polyesters
vary in properties from low melting amor-
phous substances to high melting readily
crystallizable materials. In many instances,
these materials cannot readily be plasticized
by the usually employed techniques. For
example, incorporating the plasticizers in the
20 monomers from which these polyesters are
made and then polymerizing the monomers does
not give plasticized products, as it does in cer-
tain vinyl resin plasticization processes, because
the high molecular weight polyesters are pre-
25 pared by esterification reactions or by the ester
interchange method. The materials used as
plasticizers would enter into such reactions
and actually become a part of the polyester
molecule instead of acting as a plasticizer for
30 the polyester. With respect to the linear aro-
matic polyesters having very high melting
points, i.e. above 160° C., they cannot be
plasticized by the usual methods of plasticiz-
ing high molecular weight materials. For
35 example, such materials cannot be plasticized
on a mill or in a Banbury internal mixer by
adding the liquid plasticizer to the polymer and
masticating at the temperatures available in
these machines. These polyesters, being high
40 melting and highly crystalline, and generally
possessing rapid rates of crystallization, either
do not accept the plasticizer or, before the
plasticizer can be incorporated into the poly-
mer, crystallize to form hard materials that
45 cannot be worked in these mixing machines.
Heretofore no satisfactory method has existed

for plasticizing all of the various linear aro-
matic polyesters.

According to this invention high molecular
weight linear aromatic polyesters having 50
melting points or softening points above room
temperature, and, particularly, crystallizable
linear aromatic polyesters having melting
points above 160° C., are plasticized by
adding plasticizer to the molten polyester and
55 mixing the materials together at a temperature
above the melting point of the polyester until
a homogeneous mass is obtained. The term
"high molecular weight polyesters" is used
in this specification and the appended claims 60
to mean those polyesters having an intrinsic
viscosity of at least 0.40 when measured at
30° C. in a solvent composed of a 60/40 w/w
mixture of phenol and tetrachloroethane.
Intrinsic viscosity is used as a measure of the 65
degree of polymerization of the polyester and
can be calculated using the Billmeyer
extrapolation equation:—

$$[\eta] = \frac{\eta_{sp}}{C} + \frac{\log_e \eta_r}{C}$$

in which $[\eta]$, intrinsic viscosity, is the limit 70

$$\lim_{\eta_{sp} \rightarrow 0} \frac{\eta_{sp}}{C}$$

$$\eta_{sp} = (\eta_r - 1)$$

viscosity of solution

$$\eta_r = \frac{\text{viscosity of solvent}}$$

and C is the concentration in grams of the
polyester per 100 cc. of the solution. 75

The following example illustrates the pro-
cess of this invention, the copolymer consti-
tuent proportions being given in mol per
cent:—

EXAMPLE A.

80 One thousand and fifty grams of a 60/40
ethylene terephthalate/ethylene isophthalate
copolyester were prepared by the ester inter-
change method. Immediately after the poly-
merization reaction was completed and while 85
the polyester was still molten 200 grams of a

plasticizer mixture containing 50% by weight of diethoxyethylphthalate and 50% by weight of butylbenzylphthalate heated to a temperature of about 200° C. were added to the molten polyester and the mixture was stirred for 15 to 20 minutes at approximately 250° C. The polyester-plasticizer mixture was extruded from the reactor and cooled. The resulting composition was flexible, relatively soft and had the general properties of a plasticized resin.

The above example illustrates the invention as applied to a 60/40 ethylene terephthalate/ethylene isophthalate copolyester. The process is also applicable to other linear aromatic polyesters. The term "aromatic polyester" whenever employed in the specification and claims is intended to mean a polyester in which the recurring structural unit contains an aromatic nucleus. Examples of aromatic polyesters are the polyesters derived by the self-condensation of hydroxy acids such as para-(beta-hydroxy ethoxy) benzoic acid, para-(hydroxy methyl) benzoic acid, and para-(beta-hydroxy ethyl) benzoic acid. Further examples are polyesters derived from the condensation of dicarboxylic acids such as terephthalic acid, isophthalic acid, 1,4-diphenoxy benzene-4',4''-dicarboxylic acid, 1,4-bis-(phenoxy methyl)-benzene-4',4''-dicarboxylic acid, (phenoxy methyl)-benzene-4,4'-dicarboxylic acid, phenoxy benzene-4,4'-dicarboxylic acid and diphenoxy alkane dicarboxylic acids with glycols such as ethylene glycol, trimethylene glycol, tetramethylene glycol and hexamethylene glycol. Further examples are polyesters derived from dihydroxy aromatic compounds such as hydroquinone and a dicarboxylic acid. Suitable derivatives of the acids such as the amides, acid chlorides, and the esters such as the methyl, ethyl, propyl, butyl, amyl and phenyl ester can be used. Various copolyesters from these and similar reactants can also be used. The polyesters derived from terephthalic acid and isophthalic acid or ester-forming derivatives thereof with a glycol, and terephthalate-isophthalate copolyesters constitute a preferred class. The invention has particular utility in its application to polymeric ethylene terephthalate and ethylene terephthalate-isophthalate copolymers.

The method has particular value and utility with those high molecular weight linear polyesters having melting points above about 160° C. A preferred group of polyesters to which this invention can be applied is the group of polyesters derived from terephthalic acid or isophthalic acid or mixtures thereof especially the ethylene glycol esters, and particularly those containing 70% or more of terephthalate linkages in the polyester chain.

Any plasticizer can be used in this invention which is compatible with and has plasticizing action on the particular aromatic

linear polyester. In general, it is preferred to use a plasticizer which is liquid at room temperature, but for some applications a material which is a solid at room temperature, but liquid at the melting temperature of the polyester, can be used. It is preferred that the plasticizer be in liquid state when added to the polyester. Representative examples are the ether esters of phthalic acid, such as dimethoxyethylphthalate, diethoxyethylphthalate and diethyleneglycol monoethylether phthalate, the glycolate esters of phthalic acid such as methylphthalylmethylglycolate and ethylphthalylethylglycolate, and aralkyl and aromatic esters of dicarboxylic acids, such as butylbenzylphthalate, diphenylphthalate and dibenzylsebacate, tetrahydrofurfuryl esters of dicarboxylic acids, such as tetrahydrofurfuryl adipate and tetrahydrofurfuryl sebacate, the aromatic and mixed aliphatic-aromatic esters of phosphoric acid, such as tricresylphosphate, cresyldiphenylphosphate, and methyl-diphenylphosphate, the sulfonamides such as N-ethyl-o-toluenesulfonamide, and N-ethyl-p-toluenesulfonamide, and the aralkylethers such as bis-(dimethylbenzyl) ether.

Example A has illustrated the invention as it is applied to preparing a plasticized resin from the polyester immediately after it has been made. While this is a preferred embodiment of the invention, these polyesters can also be plasticized by heating solid polyester to a temperature above its melting point and then adding the plasticizer and mixing it into the polyester. It is preferred to have the plasticizer at a temperature above the melting point of the polyester when the addition is made. This allows for addition of the plasticizer at a faster rate, and avoids any solidification of the materials due to a lowering of the temperature in the mixing vessel by the addition of cold plasticizer.

While certain representative embodiments and details have been shown for the purpose of illustrating the invention, it will be apparent to those skilled in this art that various changes and modifications may be made therein without departing from the scope of the invention, as defined in the appended claims.

Reference is made to copending Applications 1681/56 and 1682/56 (Serial Nos. 805,586 and 805,587) as setting forth inventions in the carrying out of which the process of the present invention may be employed.

WHAT WE CLAIM IS:—

1. A method of plasticizing a linear aromatic polyester which includes the step of adding a plasticizer in liquid form to hot molten polyester and mixing the polyester and plasticizer together until a homogeneous mass is obtained.
2. A method according to Claim 1 in which

the linear aromatic polyester has a melting point above 160° C.

3. A method according to Claim 1 or 2 in which the linear aromatic polyester is derived
5 from terephthalic acid and/or isophthalic acid.

4. A method according to any of Claims 1 to 4 in which the polyester and plasticizer are mixed together until a homogeneous mass is obtained, and the mixture then cooled until
10 it solidifies.

5. In the process of preparing a linear aro-

matic polyester by an ester interchange reaction followed by condensation reaction, the improvement which comprises adding a plasticizer at a temperature above the softening
15 point of the polyester to the hot, freshly prepared polyester.

6. A method of plasticizing a linear aromatic polyester substantially as set forth and described hereinbefore.
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